

DIFFUSE REFLECTANCE INFRARED SPECTROSCOPY STUDIES  
OF THE AIR OXIDATION OF COAL SURFACES

E. L. Fuller, Jr. and N. R. Smyrl

Oak Ridge National Laboratory(\*)

Oak Ridge, TN 37831-2008

INTRODUCTION

Oxidation of coals is of concern to those interested in the weathering that begins as soon as the mined material is wrested from the humid, reducing, pressurized environment of the underground seam. The loss of energy content comprises an obvious economic impact to combustion processes. Floculation and coking processes are both deleteriously effected whereas systematic information regarding the structure and reaction mechanisms can be obtained. This work is directed primarily to defining the surface structures and mechanisms occurring at the air/coal interface.

EXPERIMENTAL

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopic analyses provide a wealth of information related to the chemical changes wrought in air oxidation of coals, as noted in the spectra of Figure 1. These spectra were obtained by direct observation of an aliquot of powder subjected to the temperature and chemical treatment in the reactor that resides continuously in the analytical beam in the DRIFT attachment within the infrared spectrometer. Detailed descriptions of the equipment and techniques have been reported elsewhere<sup>1,2</sup>. Each spectrum is presented in the  $\text{Log}[R(\text{sample})/R(\text{reference})]$ , "absorbance", format as noted in reference number 1. No numerical values are reported since they are not needed for the qualitative analyses discussed in this report.

RESULTS AND DISCUSSION

Examination of the spectra elucidates several features related to the mechanism of the oxidation of the powder surfaces:

(A) The oxidation progressively consumes the aliphatic hydrogen as witnessed in the loss of characteristic absorbance in the 3000-2800 wavenumber region, generally associated with interaction of the electromagnetic energy with the resonance  $\text{-C-H}$ ,  $\text{-CH}_2$  and  $\text{-CH}_3$  stretching vibrations.

(B) Simultaneously there is an insertion of oxygen into the carbonaceous substrate to form carbonyl groups manifesting a marked enhancement of absorbance in the 1900-1600 wavenumber region, long known to be associated with the  $\text{C=O}$  vibrational

modes.

(C) The band at ca. 1550 wavenumbers due to the O-C-O and/or C-O-C bending mode is enhanced due to the oxygen enrichment of the coal structure in the surface regime penetrated by the reflecting infrared beam (see also Figure 2) In addition, the stretching vibrations of carboxylate salts are known to be manifest in absorption in this energy regime.

(D) The triplet at ca. 800  $\pm$  50 wavenumbers (due to the out-of-plane bending mode of aromatic C-H) becomes less prominent due to the loss of "aromatic" character of the oxidized material. The residual doublet in this region is much akin to the lattice modes of kaolinitic clays, consistent with the hydroxyl bands noted below in (E).

(E) The broad triangular-shaped band 3600-2000 wavenumbers remains relatively unchanged, indicating relatively little or no change in the amount and/or distribution of hydrogen bonded O-H (phenolic, alcoholic, acidic, aquatic, etc.). The narrow bands (3600-3500 wavenumbers) of the clay mineral hydroxyl groups do become more distinct as the 3500 wavenumber feature is broadened.

(F) The "aromatic" C-H band does not seem to be appreciably attacked by the oxygen treatment. Previous workers have generally attributed the band at 3000 to 3200 to an "aromatic" C-H vibrational mode. The peak value appears to shift from ca. 3050 to 3080 wavenumbers as aliphatic (-C-H) and olefinic (=C-H) entities are consumed. This is a tentative interpretation since the effect may involve another distinct type of aromatic C-H entity, not yet defined at this point in time.

Few, if any, techniques are individually able to provide as much information related to the oxidation of coals as does the in situ DRIFT technique. Additional quantitative data will be presented using the analytical techniques developed previously<sup>1</sup>.

These qualitative analyses are extremely informative and valuable in elucidating the process of weathering and resultant ramifications related to the processing of coals<sup>3</sup>. In addition a more detailed understanding is obtained by examining the difference spectra, depicting the changes induced with respect to the initial (unoxidized) material. Each of the difference spectra were obtained by direct subtraction without any arithmetic adjustment for sample size, geometric variations, etc. that are present in other more classical infrared techniques<sup>1</sup>. By presenting the data in absorbance format (rather than Kubelka-Munk or remission units) we note that we have a distinctly direct radiometric comparison to the reference material (rather than each mathematically ratioed to a diffusely reflecting reference material, KBr, CsI, NaCl, etc). The spectral changes can then be

observed in their own right on a much expanded scale and with a much more realistic interpretable background base line as noted in Figure 2. Now we can observe not only more accurate measures of the enhanced absorbance and more precise peak locations, but also delineate the progressive increase in the population of four (if not five) discrete carbonyl species based on observed inflection points in the curves formed by connecting the data points comprising the spectra.

These results are consistent with the successive oxygen insertion to form (1) aldo/keto groups, (2) acido groups, (3) acid anhydro groups, and finally (4) carbonato groups all as precursors to the ultimate release of the oxidized products of carbon dioxide and carbon monoxide. Earlier work at 400 C showed similar results albeit with faster rates<sup>1</sup>. In this work we note that the spectral distribution after 400 C oxidation differs from the 200 C result in additional transformation of the low wavenumber intensity to enhance the higher wavenumber bands (see Figure 3). This indicates that there is a greater mobility of the acido groups at 400 C to allow requisite juxtaposition of two precursors subsequent to expulsion of molecular water (dehydration) concomitant to the condensation to form the surface anhydride. This condition is contrasted to the homogeneous reactions in gas phases and/or liquid states where each of the reacting entities is completely mobile and the only activation barrier involves the energy to scission sigma bonds. A schematic representation of the surface reaction is presented below:



The initiation of the reaction requires enough energy to bring the acid entities to within a distance approaching "a" as well as the scission of both a C-O bond and an O-H bond either separately or in concert. Oxidation at 300 C yields intermediate results as shown by the 1810 and 1850 wavenumber feature in Figure 4. The results at 125 C show very little absorbance at 1850 wavenumbers, as revealed in the data of Figure 5. Subsequent elevation to the isothermal oxidation at 400 C is required to form the anhydro species. In view of the observations on more mobile configurations, "Phthalic acid melts with decomposition to the anhydride at temperatures ranging from 200 to 230°, depending on the rate of heating and the condition of the glass capillary surfaces."<sup>4</sup> This citation exemplarily refers to the bond

cleavage impediment with little or no migration barrier to the anhydride coalescence. The slight inflection at ca. 1850 wavenumbers is probably due to the small concentration of acid sites formed by oxidation of adjacent susceptible sites on the coal substrate. The migration of more dispersed acid entities is brought about only at the higher temperatures.

Further details and substantiation of the mechanisms are derived from the data of Figure 6. Here we note that the prolonged reaction at 125 C involved only minor amounts of water loss and the DRIFT spectra reveal marked loss of water due to the additional thermal activation to 400 C. These results are still of a qualitative nature but show the benefits of detailed examination to aid in our understanding of the oxidation of coals as related to the important chemical weathering processes, and precursor states to combustion at much higher temperatures.

Our project continues to develop the methodology and technique to acquire more details and more quantitative data. These results are for a single sample of a subbituminous coal from the Wyodak mine of the Roland/Smith seam, Gillette, Wyoming. Even this sample is unique in that it was acquired from a freshly opened mine face, hermetically sealed in a light tight container and maintained at 25 +/- 3 C prior to these analyses. Additional studies on "real" materials will aid in there description with respect to our "reference" materials. Not to mention, the need to apply the versatile DRIFT technique to coals of other ranks. This work extends the affirmation, "Clearly, diffuse reflectance has overwhelming advantages in the characterization of high rank coals."<sup>5</sup> to a much broader extent. The major benefits arise from 1. ease of sample preparation, 2. reactions monitored without impediment of matrix (ie. KBr), 3. measurements possible in reaction medium (not inert gas as in photoacoustic), 4. reference spectrum acquired in vacuum, 5. inherently nondestructive (allows other supporting analyses on same aliquot), 6. the ability to acquire spectra over a wide range of temperatures (77 to 800 K, at present), and 7. direct measurements in either static (batch) or flowing (continous) modes. The additional information provided by the DRIFT techniques relies on the vast amount of information obtained over the years via the more arduous classical procedures.

#### SUMMARY

Air oxidation of this sub-bituminous coal proceeds via oxygen insertion into the organic substrate progressively forming aldo/keto groups, acid groups and acid anhydride entities while consuming the hydrogen of the aliphatic hydrocarbon entities. The amount of anhydride is limited (a minority of the total oxidized sites), and serves to measure the number or adjacent susceptible sites on the coal surface. Above ca. 200 C there is sufficient activation to impart the mobility to allow the acid functionalities to come together and dehydrate to form the condensed anhydride species. Above 400 C the anhydro groups

predominate in the steady state production of carbon dioxide and water vapor. These studies show the merits of the in situ, real time DRIFT techniques for the unique definition of the chemistry and structure of coals.

#### REFERENCES

1. E. L. Fuller, Jr., N. R. Smyrl, and R. L. Howell, Chemistry and Structure of Fuels: Reaction Monitoring with Diffuse Reflectance Infrared Spectroscopy, in "Chemical, Biological and Industrial Applications of Infrared Spectroscopy" edited by James R. Durig, Wiley-Interscience, 1985.
2. E. L. Fuller, Jr. and N. R. Smyrl, Chemistry and Structure of Coals: Diffuse Reflectance Infrared Spectroscopy Equipment and Techniques, FUEL, 64, 1143-1149, (1985).
3. E. L. Fuller, Jr. and N. R. Smyrl, Diffuse Reflectance Infrared Fourier Transform, DRIFT, Studies of Coal Preparation Techniques (Preliminary Results), ORNL/CF-88/27, March 1988.
4. L. F. Fieser and M. Fieser, "Organic Chemistry" D.C. Heath and Co, 1944, p670.
5. P. Painter, B. Bartges, D. Plasizynski, T. Plasizynski, A. Lichtus, and M. Coleman, "Novel Methods for FTIR Analyses of Coal" ACS Fuel Chem. Prep. 31 65 (1986).

(\*) Operated by Martin Marietta Energy Systems, Inc. for the Department of Energy under contract No. DE-AC05-84OR21400.

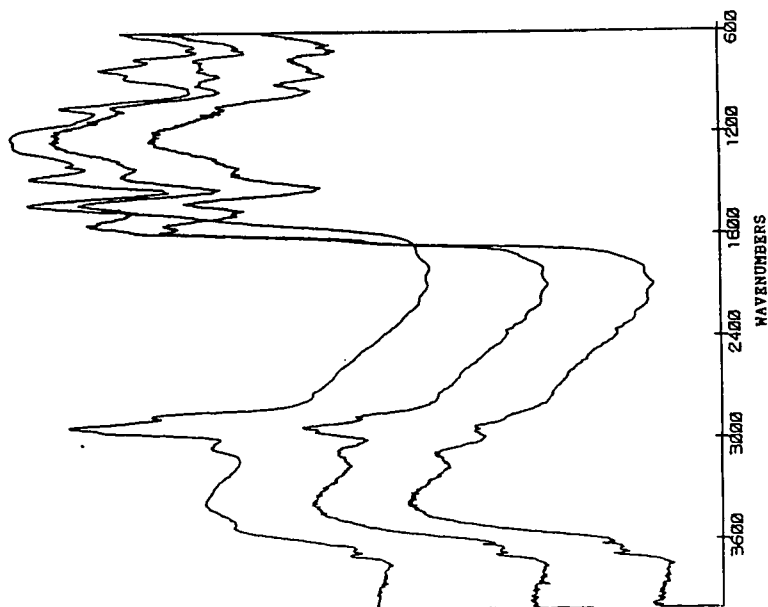


Figure 1. REPRESENTATIVE DRIFT SPECTRA FOR 200 C AIR OXIDATION OF WYODAK COAL POWDER. A. Original (unoxidized) material in vacuo, 200 C; B. 23 hours, 200 C, 100 cc/min; C. 129 hours, 200 C, 100 cc/min.

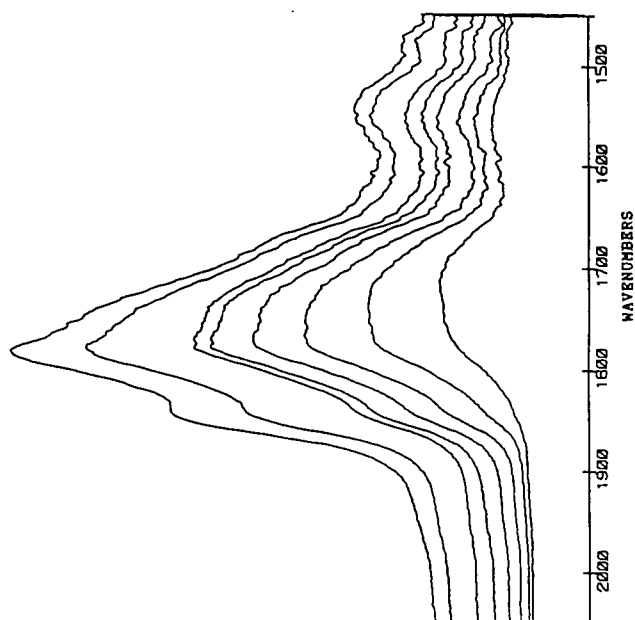


Figure 2. DRIFT DIFFERENCE SPECTRA FOR 200 C OXIDATION OF WYODAK POWDER. Successive spectra for 2, 4, 7, 10, 13, 23, 46, and 129 hours exposure (100 cc/min) isothermally in the beam of the spectrometer.

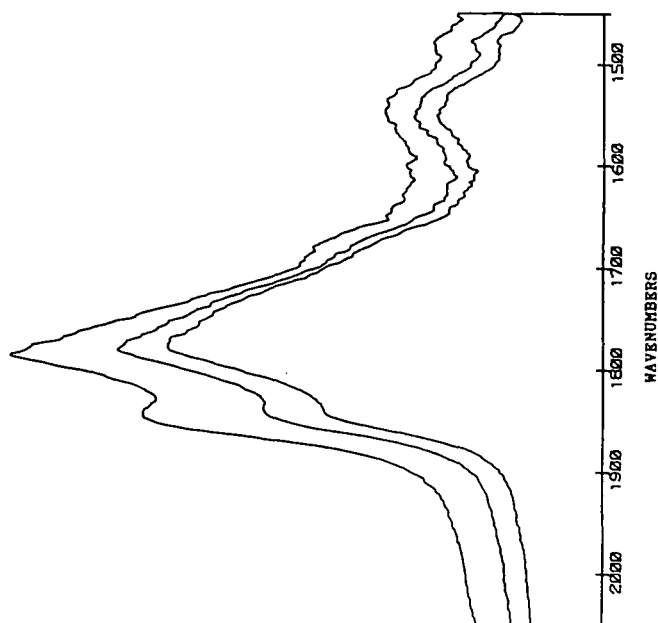


Figure 4. DRIFT DIFFERENCE SPECTRA FOR 300 °C AIR OXIDATION OF WYODAK COAL POWDER. Spectra acquired after 1, 2, and 18 hours in situ exposure to 100 cc/min air flow.

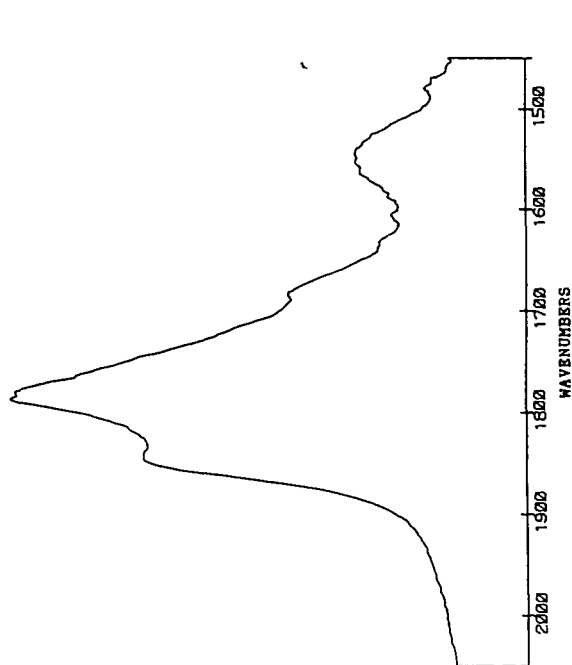


Figure 3. DRIFT DIFFERENCE SPECTRUM FOR 400 °C IN SITU OXIDATION OF WYODAK. One hour isothermal exposure at 100 cc/min flow of air through reaction cell.

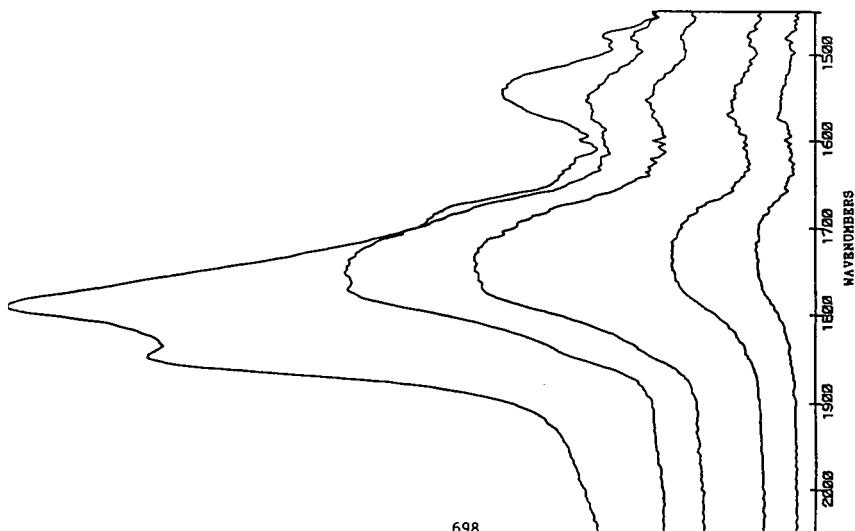


Figure 5. DRIFT DIFFERENCE SPECTRA FOR 125 C ISOTHERMAL OXIDATION OF WYODAK COAL POWDER AND SUBSEQUENT 400 C. Spectra acquired after 24, 48, 124, and 188 hours at 125 C where steady state conditions prevail. The uppermost curve was acquired after an additional 17 hours isothermal reaction at 400 C at the same 100 cc/min delivery of air reactant.

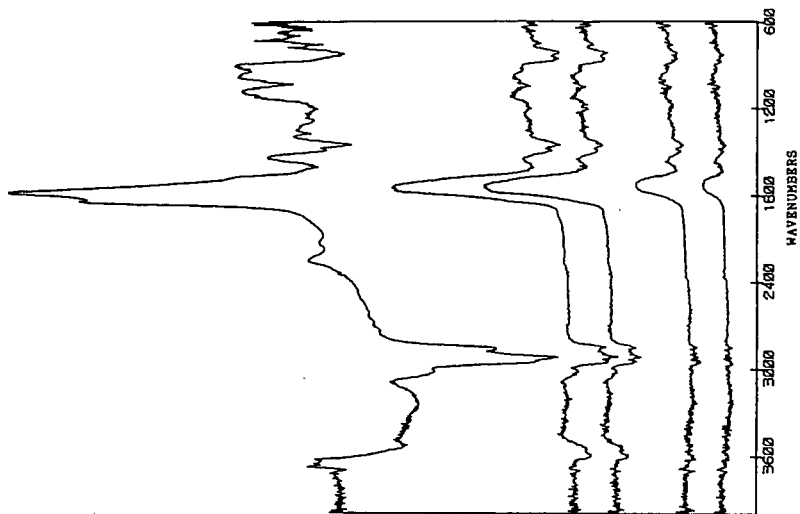


Figure 6. ENTIRE DRIFT DIFFERENCE SPECTRA FOR THE 125/400 C AIR OXIDATION OF WYODAK COAL POWDER. The relevant data are presented in Figure 5. Low temperature oxidation proceeds to the organic acid state and subsequent higher temperatures are required to dehydrate to the acid anhydride state as the precursor to carbon dioxide formation.